MILLARD

The Hydration of Ions and the

Influence of Viscosity

on the Transference Number

of Lithium Chloride

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THE HYDRATION OF IONS AND THE INFLUENCE OF VISCOSITY ON THE TRANSFERENCE NUMBER OF LITHIUM CHLORIDE

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

E A R L   B O W M A N   M I L L A R D

ENTITLED THE HYDRATION OF IONS AND THE INFLUENCE OF VISCOSITY ON

THE TRANSFERENCE NUMBER OF LITHIUM CHLORIDE

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF   DOCTOR OF PHILOSOPHY

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THE HYDRATION OF IONS AND THE INFLUENCE OF VISCOSITY ON THE TRANSFERENCE NUMBER OF LITHIUM CHLORIDE

I. _Purpose and outline of the Investigation._ The hydration of ions has attracted the attention of chemists for a number of years, and a large amount of evidence has been accumulated to show that ions are hydrated to a greater or less extent. This evidence has been collected and summarized by Washburn[1] in his review "Hydrates in Solution: Review of Recent Experimental and Theoretical Contributions to this Problem," and need not be further discussed here.

One of the strongest pieces of evidence in favor of the view that the ions are hydrated has been obtained by transference experiments in the presence of a non-electrolyte. If at the end of such an experiment the ratio of water to non-electrolyte has changed at the electrodes, either the ions have carried water in to one electrode portion or the other, or the non-electrolyte has been carried in the opposite direction by the ions. It does not seem probable, however, that all of the widely different non-electrolytes used as reference substances in investigations of this kind should unite with the ions in the same way. Washburn[2] obtained at least qualitative agreement in his experiments on sodium chloride with three different reference substances, sucrose,

1) Technology Quarterly, **21**, 361, (1908)
2) J. Am. Chem. Soc., **31**, 563, (1906)

raffinose and arsenious acid. Moreover, these experiments
on sodium chloride, lithium chloride and potassium chloride
harmonize well with those of Buchböck[1] on hydrochloric acid.
In an experiment to be described later, a value for the
hydration of the sodium ion was obtained which is in agree-
ment with Washburn's value, but with a much smaller concentra-
tion of reference substance. Similarly, Buchböck (loc.cit.)
found that a change as large as 300% in the concentration of
the non-electrolyte was without influence on the results. If
the ions were forming complexes with the non-electrolyte, it
is evident that the concentration of the latter could not be
without influence on the results. For a further discussion
of this point, see Washburn, (loc. cit., p 347-351).

The most probable conclusion, then, is that water is
being carried with the ions in their migration toward the
electrodes.

The first part of this investigation is a continuation
of the work of Washburn, using the same method and type of
apparatus. His experiment on sodium chloride has been repeated,
and results agreeing with his were obtained at both electrodes.
The hydration of the caesium ion was determined in the same
way. The direction of water transference in a normal solution
of potassium nitrate was measured.

In the second part of this paper the influence of
large changes in the viscosity of the medium on the trans-
ference number of lithium chloride has been determined. It

1) Z. physik. Chem., 55, 563, (1906)

was necessary, for purposes of comparison, to determine the transference number of lithium chloride at 0.05 normal in pure water, since no determination has been made at 25° of this quantity. These experiments will be discussed after the details concerning them have been given.

II Purification of materials. Raffinose. Kahlbaum's raffinose was treated with hot, dry, methyl alcohol in such quantity that a part of the raffinose remained undissolved, and the clear solution was decanted from the residue. The viscous mass which separated out on cooling the methyl alcohol solution in a freezing mixture was dissolved in sufficient conductivity water to form a light syrup. This solution, while still hot, was treated with small portions of hot ethyl alcohol until the precipitate which formed just failed to redissolve. It was then warmed on a hot plate until perfectly clear, and set aside over night. The crystals which separated out on cooling were drained in a platinum crucible with a perforated bottom and whirled in a centrifuge. If a 0.1 molal solution of these crystals had a specific conductivity at 25° of more than 3×10^{-6} reciprocal ohms, the crystallization from ethyl alcohol was repeated. Two crystallizations were usually sufficient.

Lithium Chloride. Kahlbaum's lithium chloride, "zur analyse," was treated with lithium hydroxide and lithium carbonate and allowed to stand some hours. The precipitate was filtered off in a carefully cleaned alundum crucible, and the filtrate was acidified and concentrated until crystals

began to appear on the hot liquid. This solution was then
cooled to room temperature and the crystals of $LiCl.H_2O$ were
filtered out in a perforated platinum crucible and drained
in a centrifuge. Care was taken to avoid cooling the solution
below 20°, for then crystals of the dihydrate are obtained,
and these melt when placed in a dessicator in a warm room.
The chloride was recrystallized from pure water four times,
after which it was found to be neutral and to contain only
a faint trace of sodium when examined in a spectroscope.

Caesium chloride. Part of the raw material consisted
of 700 grams of Pollucite, $H_2Cs_4Al_4(SiO_3)_9$, containing about
35% of caesium. It was powdered, passed through a fine
sieve, treated with sufficient aqua regia to cover it, and
placed on the steam bath over night. The undissolved residue
was washed by decantation with 500cc of water, and extracted
a second and third time. The acid extract was evaporated to
dryness, and the residue baked to dehydrate silicic acid. It
was then taken up in water, treated with an excess of ammonia
and ammonium carbonate, and filtered. After this filtrate
had been acidified with hydrochloric acid, it was evaporated
to dryness in a casserole and the residue was baked on an
electric hot plate to expel ammonium salts. To this residue,
containing now only the alkali metals, was added about 200
grams of Kahlbaum's caesium carbonate and fifty to a hundred
grams of caesium chloride of varying degrees of purity,
obtained in the market. The whole mass was taken up in a
liter and a half of hydrochloric acid, (sp. gr. 1.12), some
nitric acid was added, and sufficient iodine to convert the

whole mass into caesium dichloriodide, $CsCl_2I$, assuming it
to be all caesium chloride. The beautiful orange-red crystals
separating out on cooling were practically free from all
metals other than caesium and possible traces of rubidium,
since none of the other alkali metals form insoluble tri-
halides and the heavy metals had been almost completely
removed by the treatment with ammonia and ammonium carbonate.
The $CsCl_2I$ so obtained was recrystallized twice from hot
hydrochloric acid and then converted into caesium chloride by
heating in a porcelain dish on an electric hot plate at a
low temperature until the iodine monochloride had been
completely expelled and the residue was perfectly white. The
chloride was recrystallized twice, each time using centrifugal
draining, and was then dried at 150°. Examination in a
spectroscope showed it to be free from other alkalis with
the exception of a trace of sodium. A portion of the material
was again converted into dichloriodide, twice recrystallized
from hot hydrochloric acid, changed to chloride by heating
and again twice recrystallized. The faint sodium line was
still present, so that this metal must have come from the
glass vessels in which the crystallization was carried out.
Since it was to be used in a glass apparatus, an attempt at
further purification seemed unnecessary.

The remarkable statement by Bailey[1] that caesium
chloride is volatile with steam attracted the writer's atten-
tion, and seemed worthy of a little investigation. Accordingly,
three distilling bulbs, such as are used in Kjeldahl distilla-

1) J. Chem. Soc., 65, 445, (1894).
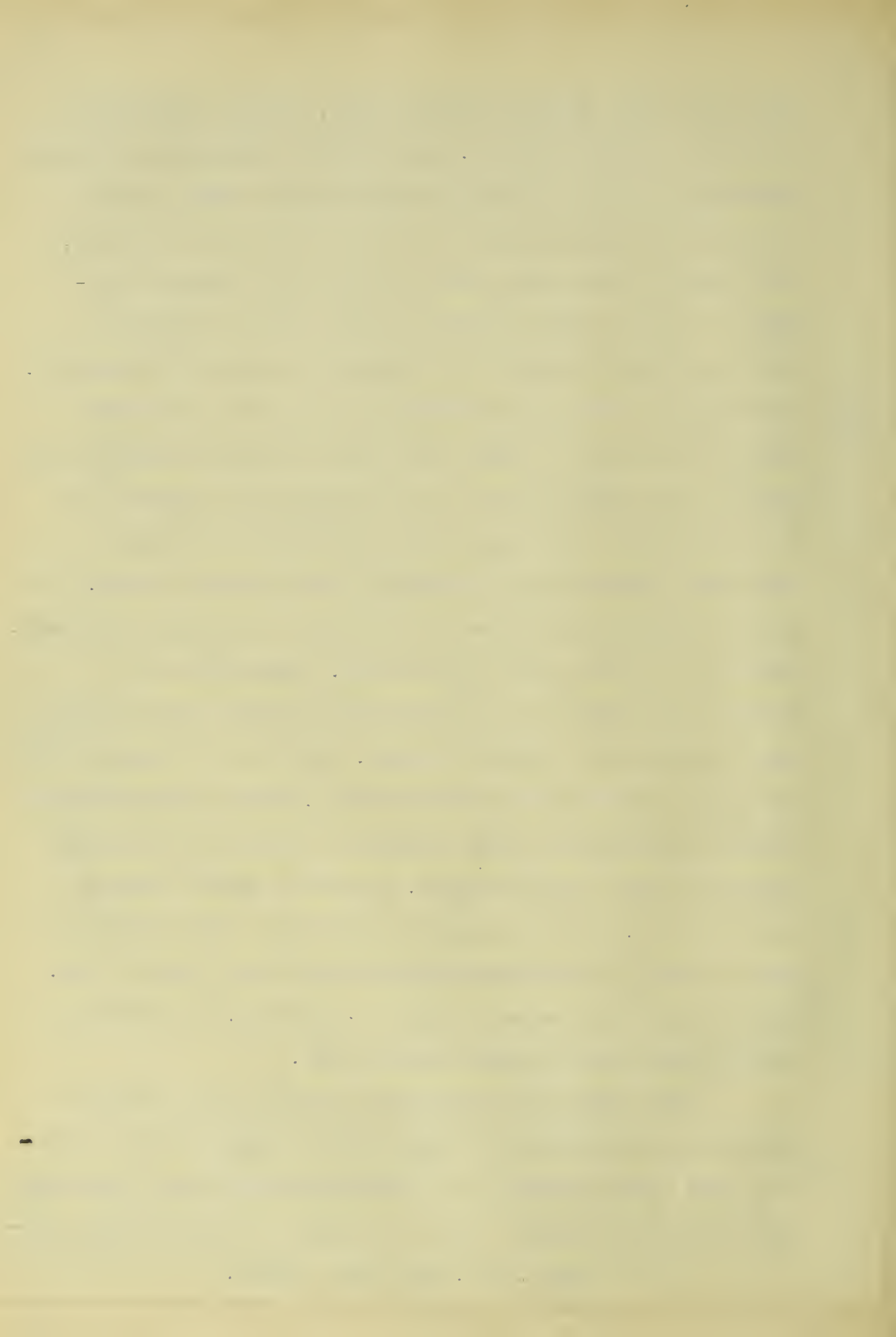
tions, were fused together in a straight column. These were used to connect the distilling flask to a carefully cleaned condenser. The distance from the surface of the boiling liquid to the condenser was about 50 centimeters. A solution composed of 5 grams of caesium chloride and a liter of water was placed in the flask and distilled until only a few cubic centimeters of liquid remained in the flask. The distillate was collected in five portions, and each was carefully tested with nitric acid and silver nitrate. Not the slightest trace of precipitate was obtained in any of the portions. The experiment was repeated a second and third time, using slightly different pieces of apparatus, but no trace of chloride was ever found in any portion of the distillate, even on long standing, when precautions were taken to prevent mechanical carrying over of caesium chloride. Bailey's experimental method must have been at fault.

Potassium nitrate. Kahlbaum's best grade was recrystallized four times from conductivity water.

Silver nitrate. This salt was recrystallized three times from conductivity water.

Water. All of the water used in preparing the solutions, in the purification of materials and the analytical operations was obtained from the special still[1] in this laboratory. Distillation took place from an alkaline permanganate solution and a liberal portion of the distillate was rejected before collecting water for use. It was collected and pre-

1) The form of this still is described by Noyes and Coolidge, Proc. Amer. Acad., 39, 190, (1903).

served in well-seasoned "non-sol" glass bottles. The specific
conductivity at 25° was always less than 1×10^{-6} reciprocal
ohms.

III Apparatus and Method of Proceedure. For the
strong solutions, the apparatus designed by Washburn[1] was
used without alteration. A diagram and photograph of it are
shown herewith. For the dilute solutions an apparatus of the
same form, but of much larger cross section (5 cm) and
containing no stop cocks, was used. A membrane of silk
gauze was used just below the anode in the larger apparatus,
since stirring always took place in this apparatus when no
membrane was used. This membrane was so far from the point
where the anode portion ended that any selective transmission
of the ions could not have affected the middle portions.
Furthermore, it is inconceivable that selective transmission
could take place through a membrane whose meshes were as
large as 0.01 mm. No membranes of any kind were used in
the apparatus for strong solutions.

A constant temperature of 25.00^o was maintained
during the experiment by immersing the whole apparatus in a
thermostat whose temperature variations were never more than
0.01^o. The electrical connections to the apparatus were care-
fully insulated from contact with the water of the bath by
good rubber tubing, which was tightly fastened over the ends
of the apparatus and made water tight by painting with
paraffin.

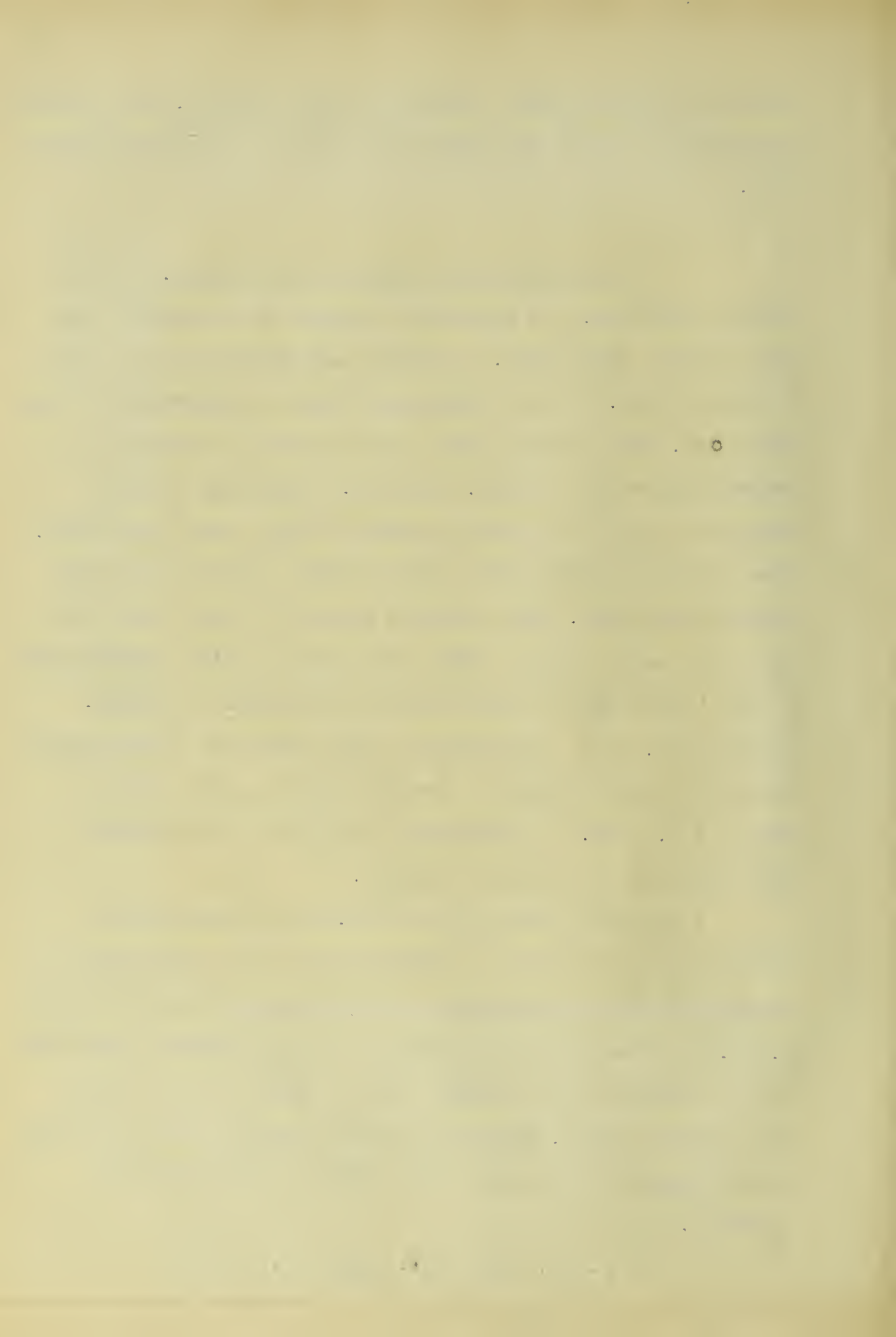1) J. Am. Chem. Soc., 31, 322, (1909)

Figure 1

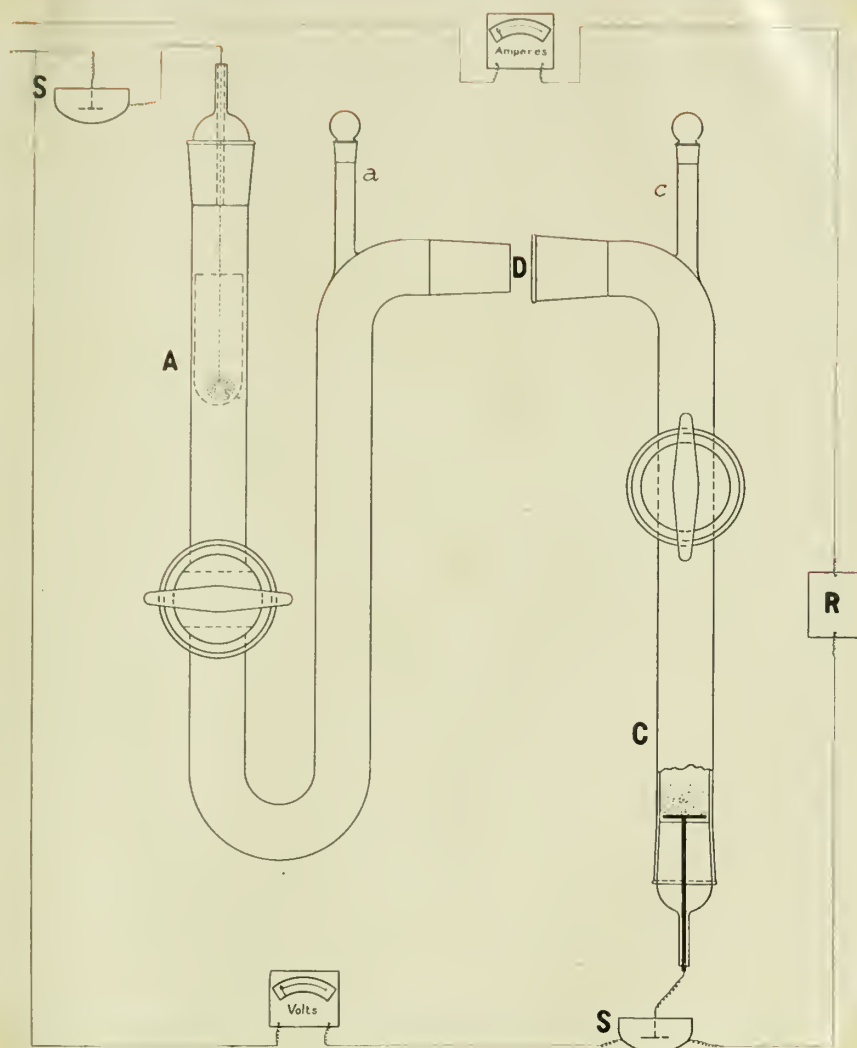Transference apparatus and stand.

Figure 2

Diagram of apparatus and connections

Coulometers. The silver coulometers were of the usual type, the cathode consisting of a platinum dish of about 100 cc capacity and the anode of a silver disc, made by fusing electrolytic silver crystals. A carefully cleaned alundum crucible replaced the usual filter paper around the anode. Freshly prepared 10% silver nitrate solution was used as the electrolyte. No portion of the electrolyte used in a coulometer was used a second time.

The ammeter in the circuit was used only to insure a constant current throughout the progress of an experiment. The amount of electricity passed through the apparatus was determined from the increase in weight of the coulometers, never from readings of the ammeter.

Electrodes. The silver chloride cathode consisted of a silver disc on which a coating of silver chloride had been deposited, covered with the required amount of silver chloride. The details of the preparation of this electrode have been given in full by Washburn, (loc. cit., p 331) and need not be repeated here. The anode consisted of a filter paper extraction thimble into which electrolytic crystals had been loosely packed around the silver wire which was connected to the electric circuit. The thimble was always perforated with numerous pinholes before being inserted in the apparatus, to allow a free circulation of the anode liquid around the electrode. In some of the experiments on dilute solutions an anode composed of coils of silver wire was used. This gives sufficient silver surface for the small amount of silver chloride formed in these experiments.

The method of proceedure with the strong solutions differed in no essential feature from that described in detail by Washburn in connection with his experiments. In the dilute solutions only two middle portions were taken, since so large a sample is required in order to obtain sufficient accuracy on the analyses. Mixing with the electrode portions would affect these two portions in opposite directions.

IV Analytical methods. Raffinose. The concentration of this substance was measured by the optical method. This method is capable of a high degree of accuracy and has the further advantage that the whole of the electrode portion can be used for the determination of the electrolyte, since the estimation of the carbohydrate does not affect the solution in any way when precautions are taken to prevent evaporation.

The polariscope used was a Schmidt and Haensch triple shade instrument of the Lippich type. Light was furnished by a small quartz mercury vapor lamp, (described in Ann. Physik, 20, 563, 1906) and was purified by passing through a spectroscope attached to the polariscope. The instrument was kept in a dark room of even temperature and was connected with a thermostat maintained at 25°, from which water was caused to circulate around the jacket of the 100 centimeter polarizing tube. The average deviation from the mean of a set of sixteen readings on this instrument

was 0.004° out of a total rotation of 55°. The same 100 centimeter tube was used in all of the optical work in this investigation. On account of the large rotation obtained by the use of such a long tube, the concentration of the reference substance was reduced considerably (30%) below that used by Washburn. It was desired to obtain results which should indicate as closely as possible the state of affairs in pure water, so that as low a concentration of reference substance as possible was desirable. The mercury E-line ($\lambda = 546.3\mu\mu$) was used in all of the polariscopic work.

For the determination of densities of the solutions, a pycnometer of the Ostwald-Sprengle type, having a capacity of 18 cc, was used. It was fitted with ground glass caps, and was counterpoised when weighed by a pycnometer of exactly the same kind. Specific gravities are at 25° refered to water at 4°. Air-free conductivity water was used in determining the water value of the pycnometer, and all weights were reduced to vacuo. The error in specific gravity determinations never amounted to more than 0.01%.

All of the solutions containing raffinose were prepared on the same day that the experiment was made, and were filtered through hardened filters to insure the absolute clarity which is so necessary for accurate polariscopic work.

The electrolyte. The chloride in the solution was determined by precipitating it from a weighed amount of the solution with an excess of pure silver nitrate solution, and collecting on a gooch crucible the precipitated silver chloride. The precipitate was washed four or five times with 0.02 normal silver nitrate solution and once with very dilute, ice cold, nitric acid before transfering to the crucible. The precipitate was transfered to the crucible wholly with nitric acid. The filtrate was filtered through a tiny (3 cm) filter to retain asbestos shreds; this filter was ignited, and the asbestos found was weighed with the crucible. An accuracy of one or two hundredths of a percent. was attained in this analysis.

Potassium nitrate was determined by evaporating a weighed amount of the solution to dryness in a quartz flask of 150 cc capacity with the repeated addition of pure fuming nitric acid until all of the raffinose was burned out and the residue was perfectly white. During this evaporation the flask was heated in an electric furnace, and was never allowed to reach the boiling temperature of the solution. To hasten the evaporation, a slow stream of purified air was passed into the flask. A large tube was fused to the air delivery tube and slipped down over the neck of the flask to prevent the entrance of dust during the prolonged process of evaporation. When all of the raffinose had been destroyed, a slight excess of pure perchloric acid, which gave no residue on evaporation, was added, and the nitric acid was expelled.

Finally, the potassium perchlorate was heated to 300° until it became constant in weight, and the flask was weighed, using a similar flask as a counterpoise.

All of the weights used in this investigation had been carefully calibrated, and all weighings are reduced to vacuum.

Effect of salts on the specific rotatory power. This effect has already been determined by Washburn for LiCl, NaCl and KCl. He found that $[\alpha]_D^{25^{\circ}}$ in the presence of one mole of salt per liter was 123.08° for KCl, 123.12° for NaCl, and 123.24° for LiCl; the corresponding value in water being 123.00°. For the E-line, the values, in the order above given are: 144.64, 144.69, 144.83 and 144.55[1]. The value found by experiment in the presence of 1.2 moles of caesium chloride was 144.64, the same value as that for potassium chloride.

Viscosities. The viscosities of the solutions were measured in the quartz viscosimeter described by Washburn and Williams[2]. The time of flow was measured with a stop watch in these experiments, since a high degree of accuracy was unnecessary for the present purpose.

The following atomic weights were used: Li $=$ 6.94, Na $=$ 23.00, K $=$ 39.10, Cs $=$ 132.81, Ag $=$ 107.88, Cl $=$ 35.46.

1) Bates, Bureau of Standards Bulletin, 2, 239.

2) J. Am. Chem. Soc., 35, 737,(1913)

V. Notation.

$\alpha^{25^{o}}$ angular rotation of the plane of polarization by the solution at 25°

$d_{4^{o}}^{25^{o}}$ specific gravity of the solution at 25° refered to water at 4°

P_r per cent of reference substance in solution.

P_s per cent of the electrolyte in the solution.

Ag^c grams of silver deposited in the coulometers.

m^e total mass in grams of electrode portion.

$\Delta m_w, \Delta n_w$ increase in grams (or moles) of water in the electrode portion.

$\Delta m_s, \Delta n_s$ increase in grams (or moles) of electrolyte in the electrode portion, refered to raffinose.

$\Delta m_s', \Delta n_s'$ increase in grams (or moles) of electrolyte in the electrode portion, refered to water as at rest.

N equivalents of electricity passed through the solution

$T^c, T^a,$ true transference number of the cation (or anion)

T_H^c, T_H^a ordinary or Hittorf transference number.

Δn_w^F number of mols of water transfered from anode to cathode per faraday of electricity.

$A,$ anode portion

$M_a, M, M_c,$ anode middle, middle, cathode middle portions.

$C,$ Cathode portion.

VI – T a b l e   I.

Data and results with Sodium Chloride

Reference substance – Raffinose

Composition of the solution:

Sodium Chloride	1.12 formula weights of NaCl per 1000 grams of water
Raffinose	0.073 formula weights $C_{18}H_{32}O_{16}$ per 1000 grams of water

Applied e.m.f.   20 volts
Current   0.10 ampere
Time of run   12 hours

	A	M_a	M	M_c	C
$\alpha_{25}^{25^0}$	51.107	50.694	50.653	50.648	50.000
d_4^{25}	1.0461	1.0522	1.0522	1.0522	1.0590
P_r	3.376	3.331	3.330	3.330	3.264
P_s	5.0467	5.9262	5.9250	5.9263	6.8703
A_c^c	5.6694				5.6699
m^e	120.23				108.99
Δn_w	- .58				.98
Δn_w	- .032				.054
Δm_s	-1.1605				1.1555
Δn_s	- .01958				.01976
$\Delta m'_s$	-1.1221				1.0915
$\Delta n'_s$	-'.01919				.0187
N_c	.05255				.05255
$T_a^c = -\Delta n_s/N$	.377				.376
T_a^a	.623				.624
T_H^c	.365				.355
T_H^a	.635				.645
$\Delta n_w/\Delta n_s$	1.6				2.7
Δn_w^F	.61		Mean 0.82		1.04

VII T a b l e II

Data and results with Caesium Chloride
Reference substance – Raffinose

Composition of the solution:

Caesium chloride   1.07 formula weights of CsCl per 1000 gramw os water

Raffinose   0.071 formula weights of $C_{18}H_{32}O_{16}$ per 1000 grams of water

Applied e.m.f.   20 volts
Current   0.1 ampere
Time of run   12 hours

	A	M_a	M	M_c	C
$\alpha^{25°}$	48.671	48.228	48.131	48.116	47.452
d_4^{25}	1.1105	1.1357	1.1357	1.1357	1.1642
P_r	3.0320		2.9319	2.9310	2.8197
P_{s_c}	12.077	14.772	14.770	14.750	17.713
Ag^c	5.5048				5.5044
m^e	132.58				119.77
Δm_w	−0.30				0.36
Δn_w	−0.0166				0.020
Δm_s	−4.243				4.198
Δn_s	−0.02521				0.02495
$\Delta m'_s$	−4.191				4.137
$\Delta n'_s$	−0.02491				0.02459
N	0.051027				0.051023
$T^c == \Delta n_s/N$	.494				.489
T^a	.506				.511
$T_c^c - \Delta n'_s/N$	.488				.482
T_h^a	.512				.518
$\Delta n_w/\Delta n_s$	.64				.80
Δn_w	.33		Mean 0.36		.39

T a b l e   III

Data and results with Caesium Chloride, Run 2
Reference Substance - Raffinose

Composition of the solution:

Caesium Chloride   1.10 formula weights of CsCl per 1000 grams of water

Raffinose   0.081 formula weights of $C_{18}H_{32}O_{16}$ per 1000 grams of water

Viscosity $\eta^{25}/\eta_0^{25} = 1.08$

Applied e.m.f.   20 volts

Current   0.1 ampere

Time of run   12 hours

	A	M_a	M	M_c	C
α 25^0	55.865	55.137	55.137	55.127	54.421
d_4^{25}	1.1152	1.1409	1.1409	1.1409	1.1689
P_r	3.4653	3.3433	3.3433	3.3428	3.2208
P_s	12.383	15.152	15.160	15.161	18.063
A_g^c	5.4787				5.4787
m^e					121.12
Δm_w					.25
Δn_w					.014
Δn_s					4.190
Δn_s					.02490
$\Delta n'_s$					4.147
$\Delta n'_s$					.02465
N	.050785				.050785
$T_a^c = \Delta n_s/N$					.490
T_a^a					.510
$T_H^c = \Delta n'_s/N$					.485
T_H^a					.515
$\Delta n_w/\Delta n_s$					.56
Δn_w^F	.45				.28

The anode residues were scorched in drying in this experiment, thus rendering uncertain the weight of the electrode portion.

VIII Results with Potassium Nitrate.

Several runs were made on 1.2 normal potassium
nitrate in the presence of 0.08 mols of raffinose, using a
silver chloride cathode and rejecting the anode side alto-
gether. The apparatus with stop cocks was used in these
experiments, and membranes of silk gauze were used. A cooling
coil was used at the cathode side to increase the density of
this portion and so prevent mixing. In every experiment
chloride was found in the middle portions, indicating that
mixing had taken place. On account of this mixing it did not
seem worth while to complete the analyses. In one case,
however, the solutions were analysed, and it was shown that
the ratio of raffinose to water had decreased at the cathode.
In other words, the potassium ion carries water with it to
the cathode in a potassium nitrate solution. By this experi-
ment it is definitely established that the change in the
ratio of raffinose to water is not due to a complex formed
between the chloride ion and the sugar. This constitutes a
strong piece of evidence in favor of the reliability of this
method of measuring hydration. It is to be regretted that definite
quantitative results could not be obtained by the use of a
chloride electrode.

IX - Influence of viscosity on the transference number of

L i t h i u m   C h l o r i d e

Table IV.

Data and results with Lithium Chloride in Water.

Composition of the solution:

Lithium Chloride | 0.053 formula weights of LiCl per 1000 grams of water

Raffinose | None
Viscosity | 1.008
Applied e.m.f. | 65 volts
Current | .03 ampere
Time of run | 5 hours

	A	M_a	M_c	C
P_s	0.20528	0.22383	0.22370	0.25595
Ag^c				.5254
m^e				206.94
$\Delta m'_s$				.0668
$\Delta n'_s$				.00157
N				.00488
T_H^c				.322
T_H^a				.678

No data were obtained at the anode. To remove any possible uncertainty, the experiment was repeated. The data will be found in Table V, on the next page.

Table V

Data and Results with Lithium Chloride in Water - 2

Composition of the solution:

Lithium chloride	0.05 formula weights of LiCl per 1000 grams of water
Raffinose	None
Viscosity	1.008
Applied e.m.f.	65 volts
Current	0.03 ampere
Time of run	5 hours

	A	M_a	M_c	C
P_s	.1853	.2091	.2093	.2492
Ag^c	.6621			.6623
m^e	348.82			207.63
$\Delta m'_s$	.0839			.0831
$\Delta n'_s$	.00198			.00196
N	.00614			.00614
T_H^c	.323			.320
T_H^a	.677			.680

X - Table VI

Data and Results with Lithium Chloride in 0.18 N Raffinose

Composition of the solution:

Lithium Chloride   0.49 formula weights of LiCl per
                                  1000 grams of water

Raffinose   0.18 formula weights of $C_{18}H_{32}O_{16}$ per
                                    1000 grams of water

Viscosity   1.250

Applied e.m.f.   65 volts

Current   0.03 ampere

Time of run   5 hours

	A	M_a	M_c	C
P_s	.2055	.2261	.2265	.2614
d_4^{25}		1.0280	1.0280	
Ag^c	.611			.614
m^e	375.07			221.41
$\Delta m'_s$	.0772			.0774
$\Delta n'_s$	.00182			.00183
N (mean)	.00568			.00568
T_H^c	.321			.322
T_H^a	.679			.678

T a b l e   V I I

Data and Results with Lithium Chloride in 0.27 N Raffinose

Composition of the solution:

Lithium chloride	0.045 formula weights of LiCl per 1000 grams of water
Raffinose	0.27 formula weights of $C_{18}H_{32}O_{16}$ per 1000 grams of water
Viscosity	1.41
Applied e.m.f.	65 volts
Current	0.025 ampere
Duration of run	5.5 Hours

	A	M_a	M_c	C
P_s	.1468	.1648	.1649	.1938
d_4^{25}		1.0409	1.0409	
$A\varepsilon^c$	.5454			.5442
m^e	377.93			
$\Delta m'_s$	.0692			
$\Delta n'_s$	.00163			
N	.00505			
T_H^c	.322			
T_H^a	.678			

No results were obtained from the cathode side in this experiment.

Table VIII

Data and Results with Lithium Chloride in 0.4 N Raffinose

Composition of the solution:

Lithium chloride	0.045 formula weights of LiCl per 1000 grams of water
Raffinose	0.40 formula weights of $C_{18}H_{32}O_{16}$ per 1000 grams of water
Viscosity	1.57
Applied e.m.f.	65 volts
Current	0.03 ampere
Time of run	5 hours

	A	M_a	M_c	C
P_s	.2267	.2449	.2452	.2758
d_4^{25}		1.0520	1.0520	
Ag^c	.5785			.5783
m^e	399.89			236.93
$\Delta m'_s$	.0738			.0728
$\Delta n'_s$	.00174			.00172
N	.00536			.00536
T_H^c	.324			.321
T_H^a	.676			.679

XI - Discussion of Results

The _facts_ established by this research are : (1) the electrolysis of a solution of caesium chloride, containing a non-electrolyte at low concentration, is attended by an increase in the concentration of the non-electrolyte at the anode and a corresponding decrease at the cathode, (2) Washburn's value for the hydration of the ions of sodium chloride has been confirmed, (3) the transference number of lithium chloride is independent of the viscosity of the solution. We will proceed to the discussion of these facts in the order named.

Hydration of caesium chloride. Washburn (loc. cit.) has discussed in full the question as to whether water is carried by the cation or raffinose by the anion. To the evidence in favor of the former view,-evidence in itself conclusive-- may be added two new facts. It has been shown (VIII) that the concentration of the non-electrolyte decreases at the cathode when potassium nitrate is substituted for potassium chloride as the electrolyte. On account of the mixing of the electrode portions with the middle portions in this experiment, it was impossible to determine the amount of water carried by the cation; but it seems safe to say that it was at least as great as in the experiment with potassium chloride. The mean value of Δn_W^F obtained in the experiment with sodium chloride was the same as Washburn's value, although a 35% change had been made in the concentration of the non-electrolyte used as a reference substance.

It seems scarcely probable that this could be the case if a complex between the chloride ion and raffinose were responsible for the change of concentration of the non-electrolyte.

The results obtained must, therefore, be due to the migration of water with the current; and since it has been shown[1] that the presence of the electrolyte is necessary to produce this result, it seems fair to assume the existence of some sort of a complex between water and one or both of the ions in each solution. This assumption is entirely in accord with all of the results, as may be seen from Table IX.

The equations used by Washburn in discussing his results were

$$T^c N_W^c - T^a N_W^a = \Delta n_W^F \qquad (A)$$

and

$$N_W^c = \Delta n_W^F / T^c + T^a / T^c N_w^a . \qquad (B)$$

His data for comparing these quantities are collected with those of Buchböck[2] and my own in the following table. It will be noticed that the caesium ion carries less water than any of the other alkali ions, as was to be expected, but that it carries more water than the chloride ion. Here, as with potassium chloride, the true transference number in a normal solution is identical with the value at zero concentration.

1) Washburn, l.c., p. 342.

2) Z. physik. Chem., 55, 563, (1906)

$$\text{T a b l e} \quad \text{I X}^{3)}$$

Electrolyte (Conc. 1.3 N)	n_W^F/T^C	n_W^F	T^C	T_∞^C	T_H^C
HCl	0.28 ± 0.04	0.24 ± 04	.844	.847	.82
CsCl	0.67 ± 0.1	0.33 ± 06	.491	.491	.485
KCl	1.3 ± 0.2	0.60 ± 08	.495	.495	.432
NaCl	2.0 ± 0.2	0.76 ± 08	.383	.396	.366
LiCl	4.7 ± 0.4	$1.5 \pm .1$	.304	.330	.278

$$N_W^{H^+} = 0.28 \pm 0.04 + 0.185\, N_W^{Cl^-} \qquad (1)$$

$$N_W^{Cs^+} = 0.67 \pm 0.1 + 1.03\, N_W^{Cl^-} \qquad (2)$$

$$N_W^{K^+} = 1.3 \pm 0.2 + 1.02\, N_W^{Cl^-} \qquad (3)$$

$$N_W^{Na^+} = 2.0 \pm 0.2 + 1.61\, N_W^{Cl^-} \qquad (4)$$

$$N_W^{Li^+} = 4.7 \pm 0.4 + 2.29\, N_W^{Cl^-} \qquad (5)$$

3) In this table the values given are the _means_ of the two results obtained at each electrode independently. The deviation of this mean from the two individual values is indicated in each instance. Since most of the errors peculiar to transference experiments have a tendency to make the changes at the electrodes smaller in magnitude, the deviations indicated may be considered as a fairly reliable measure of the maximum error of the results.

The quantity $N_W^{Cl^-}$ may be eliminated from equations
(2) and (3) on the previous page by subtraction, since T^a/T^c
is practically unity in each case. This leads to the relation

$$N_W^K - N_W^{Cs} = 0.65$$

or, in words, the caesium ion carries 0.65 moles of water
less than the potassium ion.

The effect of Viscosity on the transference number of
lithium chloride. Since the ions of lithium chloride are
hydrated to a very different degree, it seemed probable that
experiments on the influence of viscosity on its transference
number would be particularly interesting. As is well known,
both the viscosity and the transference number change rapidly
as the concentration of this salt is increased. The relation
between the conductance and viscosity of electrolytic solu-
tions has recently received an elaborate discussion by C. A.
Kraus[1]. I quote the following sentences from his paper, as
bearing rather pointedly on the problem at hand: "In the
case of lithium chloride, for example, the viscosity change
is due to the presence of very large neutral molecules of the
salt and, probably, also to large lithium ions. Now Washburn
has shown that the lithium ion is more highly hydrated than
the chloride ion. The lithium ion will, therefore, experience
much greater opposition to its motion than the relatively
small chloride ion. If the difference in the size of the ions
is great enough, the smaller ion will, in the limit, experi-

1) J. Am. Chem. Soc., 36, 35-65, (1914)

ence no.change whatever in resistance to motion; while the larger ion will experience increased resistance which is directly proportional to the fluidity change. It is obvious that the transference number of the ions will be affected, in this case, in correspondence with the change in the speed of the larger ion."

By correcting the conductance data of Washburn and MacInnes[1] for the viscosity influence on both ions, Kraus obtained a curve which deviated more from the Kraus equation

$$n \log (c \Lambda) = \log \left[c(\Lambda_o - \Lambda) \right] + \log D \Lambda_o^{n-1}$$

than the same data without any viscosity correction. When the correction for viscosity was applied to the lithium ion alone, a straight line was obtained for this function.

Similarly, assuming that viscosity affects the lithium ion but not the chloride ion, and that the Λ_o values for Cl^- and Li^+ are 65.5 and 33.3, Kraus calculated the transference number T^c in normal lithium chloride solution, whose relative viscosity is 1.14, as follows:

$$T^{Li}_{1.25} = \frac{33.3/1.14}{65.5 + 33.3/1.14} = 0.304$$

This value is considerable higher than the ordinary transference number obtained by Washburn at this concentration, namely 0.276, but it is practically identical with his value of the true transference number, 0.306, at this concentration.

1) J. Am. Chem. Soc., 33, 1886, (1911)

This agreement, if it means anything, is direct proof that the assumption made by Kraus is in error, for this transference number was obtained in a medium whose viscosity had been increased to about 1.40 by the addition of raffinose. Using this viscosity in his equation, we have

$$T_{1.25}^{Li} = \frac{33.3/1.40}{65.5 + 33.3/1.40} = .267,$$

a result which is <u>lower</u> than the Hittorf number in 1.25 normal solution.

The change of the transference number with increasing concentration must be influenced by some factor other than the viscosity, however. If we calculate the transference number of lithium chloride in a medium whose viscosity is 1.60 in the same manner as above, we obtain

$$T^{Li} = \frac{33.3/1.60}{65.5 + 33.3/1.60} = .242.$$

As we have seen in Table VIII, the value obtained by experiment in such a medium is 0.322, a value <u>identical with the transference number obtained in water at the same LiCl concentration</u>.

It might appear at first thought that the change of the transference number with the concentration is due to the dehydrating influence of the neutral LiCl molecules. This, however, would tend to increase the speed of the lithium ion more than the chloride ion, since it is more highly hydrated, and cause the transference number of the lithium

ion to increase. Undoubtedly both of these factors, and
possibly others, produce an effect.

Kraus, (loc. cit., p. 48) has pointed out very
emphatically that "viscosity change affects the same ions
differently when the viscosity change is brought about by
different causes." This conclusion might be confirmed by the
results obtained in the experiments, if it be assumed that
the change in the transference number of lithium chloride
with the concentration is a viscosity effect only. The pro-
ceedure of correcting only the lithium ion for viscosity seems,
however, to be unjustified, since the experiments recorded
above show no change in the relative velocity of the ions
when the viscosity is changed as much as 58%.

It is possible that the dehydrating effect of the
raffinose is just compensated by the viscosity influence,
since these two factors operate in opposite directions, but
it is rather suprising that such exact compensations could
take place at three different concentrations of raffinose.
It is not evident to the writer that this question can be
settled in any other way than by an experiment in which
dehydration is produced without changing the viscosity. For
example, if 0.3 formula weights of CH_3OH were added to a
liter of 0.05 normal lithium chloride solution, the activity
of the water in the solution would be decreased to approxi-
mately that which it has in a solution containing 0.05
formula weights of LiCl and 0.3 formula weights of $C_{18}H_{32}O_{16}$
per 1000 grams of water. The viscosity of this solution,

however, would be very nearly that of a pure aqueous solution
of lithium chloride at the same concentration. If in this
solution a transference number greater than 0.322 was obtained,
some ground would exist for assuming that dehydration and
viscosity were compensating each other in the raffinose
solutions. Such an experiment has not been performed, on
account of lack of sufficient time; it will, however, be
performed in the near future. It seems best to postpone
further discussion until the experimental data are at hand.

If the addition of as much as 0.04 formula weights of
$C_{18}H_{32}O_{16}$ per liter produces no other effect in a lithium
chloride solution than a 58% increasein the viscosity of the
medium, then the transference number is independent of the
viscosity. It is difficult to harmonize this statement with
the fact that change of conductivity with the temperature
almost parallels the change of viscosity with the temperature
unless all of the ions are affected to the same relative
extent by a viscosity change.

X I I   S u m m a r y

The following points have been established by means of transference experiments on aqueous solutions of sodium chloride, lithium chloride and caesium chloride:

(1) The sodium ion is more highly hydrated that the potassium ion, but less hydrated than the lithium ion, as was found by Washburn.

(2) The caesium ion carries much less water than the potassium ion, but more than the chloride ion.

(3) Caesium Chloride is not volatile with steam.

(4) The transference number of lithium chloride is not affected by large changes in the viscosity of the medium, at least when these changes are produced by the addition of raffinose.

(5) Water is carried toward the cathode with the potassium ion when a solution of potassium nitrate is electrolysed.

(6) The value of the hydration is independent of the concentration of the reference substance used.

(7) The statement by Kraus that viscosity affects a large ion more than a small one, seems improbable.

XIII   Acknowledgement

It is a pleasure to acknowledge my gratitude to Professor E. W. Washburn for his sympathetic interest throughout the progress of this work. His timely suggestions and criticisms have contributed largely to its successful completion.

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XIV   Biographical

The writer received his elementary and secondary
education in the schools of Boulder, Colorado. He entered the
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During the years 1911-13 he held an assistantship
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